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Application of thermogravimetry in the assessment of coatings ability to be metallized

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Abstract The main aim of this work was to assess the ability of thermogravimetric method to predetermine the surface activation properties of the coatings intended for laser-assisted electroless metallization. In this technique of metallization, surface of polymer material has to be activated before immersing in electroless metallization bath. Surface activation may consist in compositional modification of polymer material and in laser irradiation. In this work, polyurethane or epoxy coatings containing copper(I) oxide and copper(II) acetylacetonate or copper hydroxide were laser irradiated and then electrolessly metallized. Surface activation properties are evaluated usually by means of optical imaging, scanning electron microscopy, energy-dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy. In this work, an attempt was made to evaluate these properties based on thermogravimetric measurements.

Keywords Polymer coating · Laser modification · Electroless metallization · Thermogravimetry

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Introduction

The very first galvanic metallization baths for autocatalytic deposition of copper or nickel were elaborated in the 50 s of the twentieth century [1]. Currently, most of the metallized polymers are thermoplastics, of which more than 90 % are represented by poly(acrylonitrile-butadiene-styrene) [2–4]. Initially, metallization of polymers was applied for decorative purposes, but with the development of metallization methods a number of applications have significantly increased. Metallized polymers are frequently used in many fields of technology including manufacturing of electronic integrated circuits, equipment for cars, airplanes and ships. Dynamic development of electronic devices, ongoing demands for their miniaturization as well as other requirements of modern technology constitute an important stimulus for conducting basic and experimental researches in the field of polymer metallization [5–8]. In electronics, physical (PVD) or chemical (CVD) vapour depositions of thin metallic films on the polymer substrate are mainly applied [9–11]. However, chemical autocatalytic metallization is the most widely industrially applied method for polymer metallization.

The key issue in chemical autocatalytic metallization is proper activation of polymer surface. It mainly consists in covering the polymer surface with catalytic atoms, which catalyse the reduction of metal ions from metallization bath [12–14]. The most frequently applied catalyst is palladium, but copper, gold and silver are also used [15–17].

In the last years, new approach for laser-assisted electroless metallization of polymers was proposed [18, 19]. It consists in application of organic and inorganic metal compounds (precursors) into the polymer matrix at the stage of composite manufacturing, and next in laser irradiation. As a result of laser irradiation polymer matrix is

ablated, whereas heavier metal atoms extracted from precursors remain on the polymer surface and can catalyse electroless metallization [20–22].

Many specially designed polymer composites have been proposed as applicable for laser-assisted electroless metallization. However, designing, manufacturing and laser irradiation are needed to verify final ability of the composites to be electrolessly metallized. These experimental processes are time- and fund-consuming; thus, proposition of any simplified method to predetermine surface activation properties of the composites would be highly desirable. In the context of this need, thermogravimetry was proposed in this work as a very informative and promising method to predetermine surface activation properties. In general, thermogravimetry is used to determine thermal degradation and stability of various materials as polymers [23], composites [24], metal oxides [25] or complexes [26]. In this work, this technique was used to predetermine coatings ability to be directly metallized after laser surface activation. It was based on the assumption that thermal degradation is the main reason for laser-induced surface activation of polymer composites containing metallic compounds. Laser ablation (mass loss) results in the release of metal species on composite surface, which causes its activation for direct electroless metallization. More detailed analysis for this correlation will be presented further in section concerning results and discussion.

Various coatings composition was prepared and tested in order to find some relation between polymer degradation affected by heat induced by laser irradiation and during TG experiments. Polyurethane or epoxy resins were mixed with the powders of copper(I) oxide and copper(II) acetylacetonate or copper hydroxide. The coatings were tested by means of TG and further by standard procedures for evaluation of coatings ability to be electrolessly metallized.

Experimental

Materials

The following materials were applied:

- Epoxide resin, type A4089 (Haering, German); further referred to as coating E.
- Polyurethane resin, type B4060 (Haering, Germany); further referred to as coating U.
- Copper(II) acetylacetonate with formula: $[CH_3COCH{=}C(O{-})CH_3]_2Cu$; further in this work referred to as $Cu(acac)_2$ (Sigma-Aldrich, USA), molar mass 261.76 g mol^{-1}, melting temperature $T_m = 245$ °C, purity 97 %.
- Copper(I) oxide, with formula: CuO_2 (Sigma-Aldrich, USA), molar mass 143 g mol^{-1}, $T_m = 1232$ °C, purity 97 %.
- Copper(II) hydroxide, with formula $Cu(OH)_2$, (Sigma-Aldrich, USA), molar mass 97.56 g mol^{-1}, $T_m = 80$ °C, technical grade.
- Autocatalytic metallization bath, type M-Copper 85 (MacDermid, USA).
- Formaldehyde 36 %, CH_2O (POCH, Poland), molar mass 30.03 g mol^{-1}.

Processing

Coatings were prepared by mixing the resins E or U with the powders of CuO_2 and $Cu(acac)_2$ or $Cu(OH)_2$. Next injection moulded polycarbonate sheets were dip-coated within the coatings mixtures. The detailed compositions of prepared coatings are presented in Table 1.

The coatings were dried for 7 days at room temperature and afterwards irradiated with excimer laser type LPX 300 (Coherent, USA). Various number of laser pulses (5, 10, 50 or 100) at fluence of 100 mJ/cm^2 and repetition rate 5 Hz were applied. For clarity of discussion, coatings which were irradiated with different number of laser pulses were additionally designated by the number following designation of coatings (e.g. U1_100). Exact value of laser fluence was determined using power meter type FieldMax II TOP (Coherent Inc., USA). The aim of laser irradiation was to create copper agglomerates on coatings surface. Laser activated coatings could be metallized by chemical means without any additional pretreatments.

After laser irradiation, coatings were electrolessly metallized. The metallization process was performed using six-component metallization bath with formaldehyde as reducing agent. The *pH* value of the bath was 12.8 at temperature 46 °C. The samples were metallized for 60 min while the bath was aerated.

Examination

Thermogravimetric measurements were taken using thermogravimeter Q500 (TA Instruments, USA). The samples of about 10 mg were deposited in an open platinum crucible and then heated from room temperature up to 700 °C

Table 1 Composition of prepared polymer coatings

Sample	Contents/mass%		
	CuO_2	$Cu(acac)_2$	$Cu(OH)_2$
E1	15	5	0
E2	15	0	5
U1	15	5	0
U2	15	0	5

at constant rate of 10 °C/min. The experiments were conducted under nitrogen flow of 54 µl/min.

Optical imaging of copper-plated coatings was performed using standard digital camera. Performed photos clearly evidenced ability of coatings to be metallized after laser irradiation.

Scanning electron microscopy (SEM) was done using microscope type SU8010 (Hitachi, Japan). SEM images were recorded at 15 kV electrical voltage and electron current of about 65 µA. While electron beam was scanning, the samples' secondary electrons and X-ray radiation (EDX techniques) were registered in appropriate detectors. Coatings which were not plated with copper were covered with thin (2 nm) vapour deposited gold layer before SEM imaging.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy of the coatings was also performed. Final spectra have an average of 16 spectra recorded for the wavenumber ranged from 4000 to 650 cm^{-1}.

Results and discussion

Laser irradiation can initiate various chemical and physical processes within surface layer of polymer material. There are two main key parameters in laser surface treatment of polymer material. It is laser fluence (F) defined as laser pulse energy per unit area and absorption coefficient (α) of laser radiation at a specific wavelength (λ). If the laser fluence is high enough, material fragments are ejected (laser ablation). The critical value of the fluence (F^{th}) at which this process begins is called ablation threshold.

In general, the change of fluence (∂F) per change of penetration depth (∂z) of laser radiation is proportional to α and to fluence (F_0) of incidence can be expressed by Lambert–Beer law:

$$\frac{\partial F}{\partial z} = -\alpha F_0 \tag{1}$$

$$F(z) = F_0 e^{-\alpha z} \tag{2}$$

Transforming Eq. 2 depth (L) of ablation can be determined [27]:

$$L = \frac{1}{\alpha} \ln\left(\frac{F}{F^{th}}\right) \tag{3}$$

This logarithmic relationship can be graphically represented as shown in Fig. 1.

Below ablation threshold photochemical reaction as oxidation, grafting and crosslinking can occur but polymer is not ablated. However, above this value accumulated energy is high enough to initiate polymer ablation. Polymer ablation results from degradation associated with loss of polymer mass.

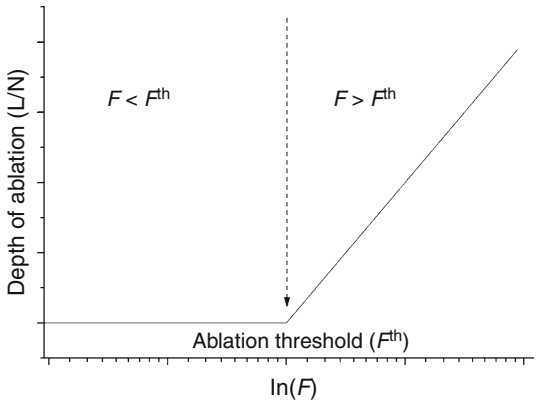

Fig. 1 Depth (L) of ablation per number (N) of laser pulses versus laser fluence

During laser ablation, some critical value of temperature (T_{max}) cannot be exceeded because excess of energy is converted into kinetic energy of ejected material fragments. This temperature can be expressed by the formula:

$$T_{max} = \alpha F^{th}/\rho \cdot c \tag{4}$$

where ρ—material density, c—heat capacity constant.

Laser ablation is necessary for surface activation of polymer composite in laser-assisted electroless metallization. Polymer fragments are ablated, while heavier metal atoms are left on the surface. These atoms can catalyse reduction of copper ions from metallization bath on the surface of polymer composite.

In general, with increasing fluence of laser radiation better effects of surface activation are obtained [28, 29]. Laser fluence is converted in heat in polymer surface layer. Induced heat causes polymer degradation and formation of low molecular weight degradation products (e.g. monomers, H_2, CO_2, CO, H_2O and O_2). This mechanism is similar to that in thermogravimetric experiments. Therefore, an idea to use thermogravimetric experiments to predetermine surface activation properties of specially designed polymer composites can be reasonable.

Thermogravimetric curves for coatings E1 and U1 are presented in Fig. 2, whereas for coatings E2 and U2 in Fig. 3.

In general, it is well seen that polyurethane coatings were more susceptible to thermal degradation than epoxide coatings (Figs. 2a, 3a) and degraded more rapidly (Figs. 2b, 3b). Because laser ablation is very dynamic process of mass removal, the data of thermogravimetric analysis which can be correlated with this process should be find for highest extrema of DTG curves. The temperatures for the main extrema of DTG curves for epoxide coatings E1 and E2 were 445 and 443 °C, respectively,

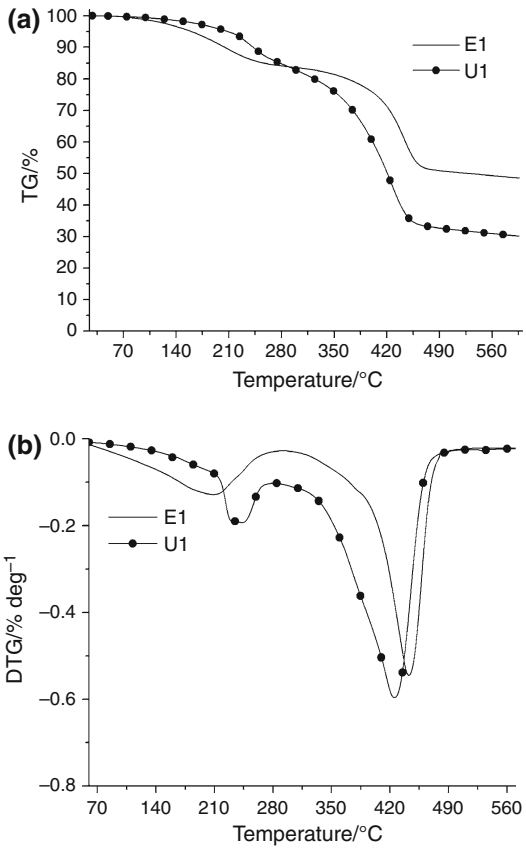

Fig. 2 Thermogravimetric curves for coatings E1 and U1

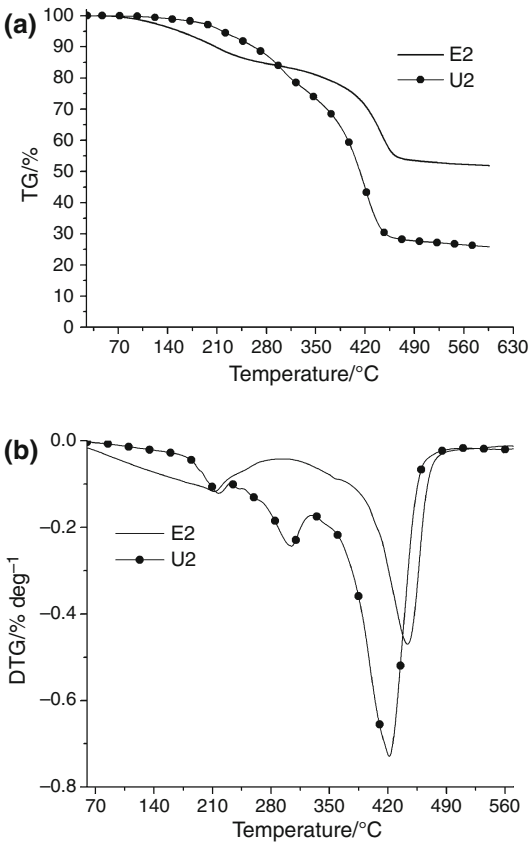

Fig. 3 Thermogravimetric curves for coatings E2 and U2

whereas for polyurethane coatings U1 and U2 were 425 and 422 °C, respectively. This slight difference can reflect better ability of polyurethane to be laser ablated than epoxide coatings. Nevertheless important are the values of DTG themselves at their extrema. For coatings E1 and E2, it was −0.55 and −0.47 % °C^{-1}, whereas for coatings U1 and U2 −0.60 and −0.73 % °C^{-1}, respectively. Thus, one can presume that laser ablation rate can be higher in case of polyurethane than epoxide coatings.

Coatings were laser irradiated and electrolessly metallized to verify the hypothesis that thermogravimetric heat-induced degradation can reflect the effects of laser-induced degradation. The effects of metallization for coatings irradiated with 50 laser pulses are presented in Fig. 4.

It can be noticed that copper layers are visible on polyurethane coatings, while epoxide coatings stayed uncovered. These results are in line with thermogravimetric measurements because epoxide coatings were more resistant to heat-induced degradation as compared to polyurethane coatings. The fact that coatings U2 are better metallized than coating U1 is also well reflected by thermogravimetric measurements. Mass loss of coating U2 was about 75 % while of coating U1 about 70 %.

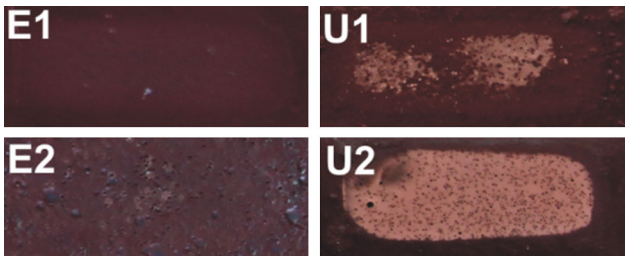

Fig. 4 Epoxide and polyurethane coatings irradiated with 50 laser pulses

The effects of surface activation between coatings U1 and U2 irradiated with various number of laser pulses are presented in Fig. 5.

It is well seen that coating U2 had better ability to be laser activated and thus electrolessly metallized. Coating U1 was more heat resistant than coating U2 as proved by TG analysis. Therefore, higher energy doses of laser radiation were needed to ablate and activate surface of coating U1 than U2.

Laser ablation of coatings caused removal of polymer matrix, whereas heavier copper atoms were agglomerated on the surface (Fig. 6).

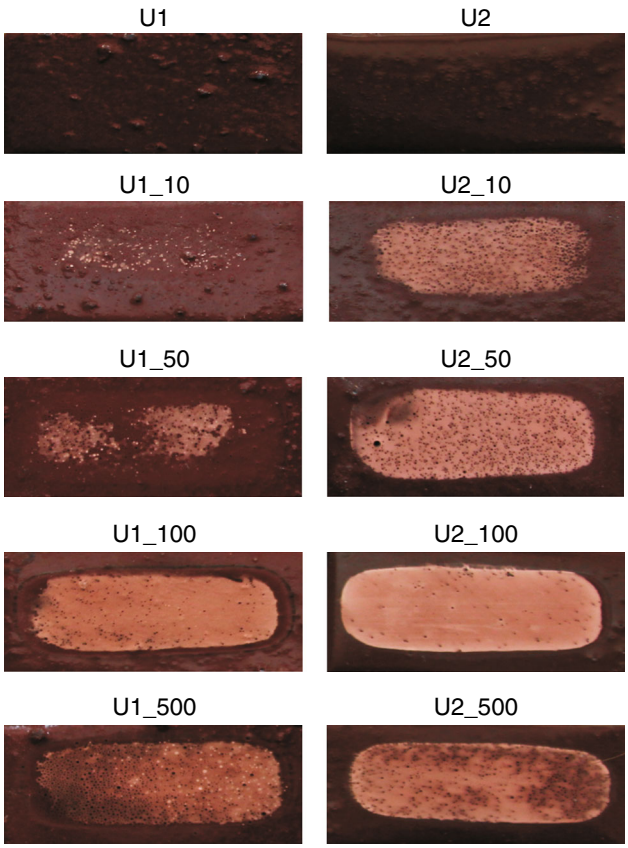

Fig. 5 Polyurethane coatings irradiated with different number of laser pulses and electrolessly metallized

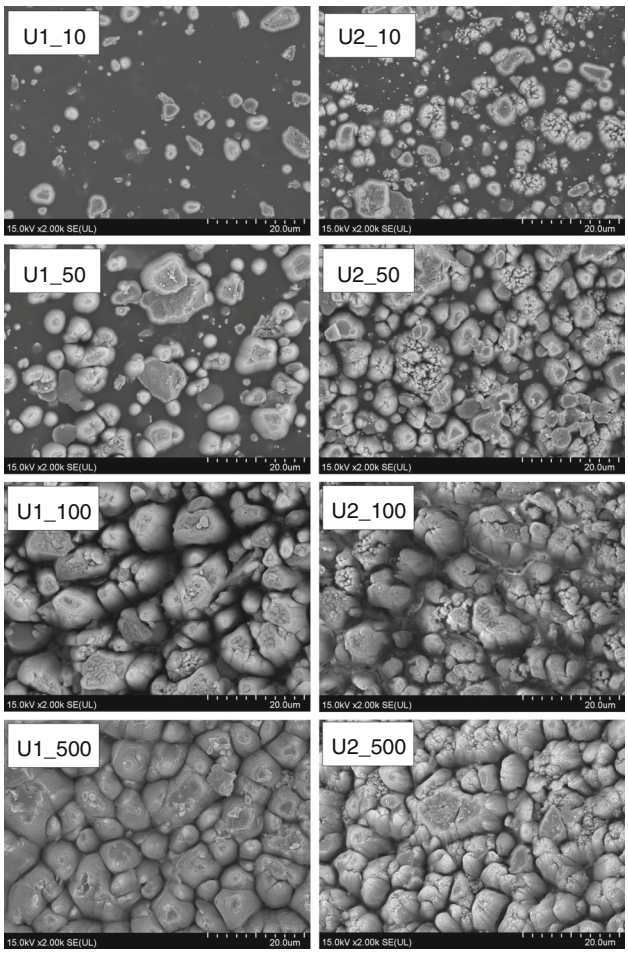

Fig. 6 Polyurethane coatings irradiated with different number of laser pulses

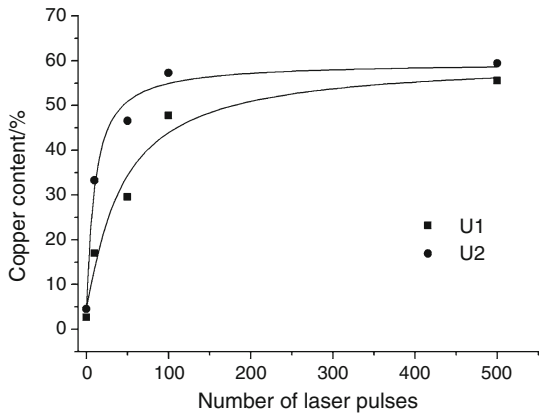

Fig. 7 Percentage content of copper atoms determined by EDX analysis

Number of copper agglomerates increased with increasing number of laser pulses (Fig. 6). It resulted from progressive ablation of polymer matrix and from reduction of copper compounds to metallic copper. Reduced copper compounds formed copper agglomerates. Copper agglomerates as resistant to laser ablation formed a mask against laser radiation for the material beneath. On the other hand, black area between the bright copper agglomerates represents cavities formed as a result of laser ablation (Fig. 6).

EDX analysis was performed to determine changes of copper content in coatings surface layer (Fig. 7). These results confirmed that more copper agglomerates were formed in coatings U2 than U1, especially at lower radiation doses (up to 100 laser pulses).

Change in chemical structure of coatings induced by laser radiation was also evaluated based on ATR-FTIR analysis (Figs. 8, 9).

The spectra at wavenumber from 4000 to 1700 cm^{-1} for coatings U1 were changing less pronounced with increasing number of laser pulses as compared to the spectra for coatings U2. The slope of the baseline increased at wavenumber 4000 cm^{-1} reaching absorbance of 0.37 for coating U2_500 and 0.27 for coating U1_500. This increase was caused by increasing roughness of ablated polymer coatings which lead to diffraction of IR radiation. Additionally, with increasing number of laser pulses a decrease in CH_2/CH_3 absorption bands (at 3000–2800 cm^{-1}) characteristic for polyurethane resin was observed. This decrease resulted from progressive

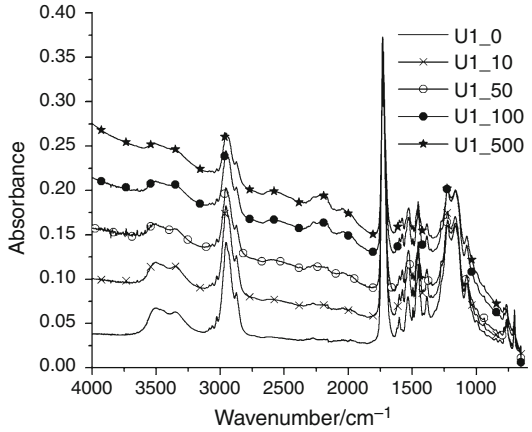

Fig. 8 ATR-FTIR spectra for coating U1 irradiated with different number of laser pulses

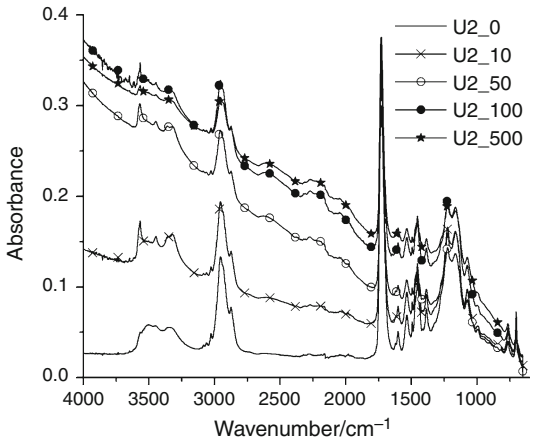

Fig. 9 ATR-FTIR spectra for coating U2 irradiated with different number of laser pulses

ablation of the polymer matrix with increasing number of laser pulses.

Conclusions

Application of lasers in electroless metallization of polymer material is very promising method. This method is currently intensively studied and developed. Its fundamental aspect is to design new compositions of polymer materials characterized with high susceptibility to electroless metallization. Therefore, new composites have to be prepared, then laser irradiated and in the final step metallized in order to prove surface activation properties. However, this is time- and fund-consuming process. As presented in this work, thermogravimetry can be informative method to predetermine composites ability to be metallized after laser modification. This measurement technique well reflects thermal degradation of polymer materials which can be compared to laser-induced polymer degradation to some extent. Application of TG can contribute to more effective designing process of new polymer composites. This, however, should be experimentally verified based on the larger series of various composites.

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References

1. Brenner A, Riddell G. Cobalt plating by chemical reduction, US Patent 2532284; 1950.
2. Li D, Goodwin K, Yang C. Electroless copper deposition on aluminum-seeded ABS plastics. J Mater Sci. 2008;43:7121–31.
3. Tang X, Cao M, Bi C, Yan L, Zhang B. Research on a new surface activation process for electroless plating on ABS plastic. Mater Lett. 2008;62:1089–91.
4. Teixeira LAC, Santini MC. Surface conditioning of ABS for metallization without the use of chromium baths. J Mater Process Technol. 2005;170:37–41.
5. Guo RH, Jiang SQ, Yuen CWM, Ng MCF. An alternative process for electroless copper plating on polyester fabric. J Mater Sci Mater Electron. 2009;20:33–8.
6. Rao Z, Chong EK, Anderson NL, Stevens MG, Driver R, Paulose KV. A tin-free catalyst for electroless platinum deposition on polyethylene terephthalate. J Mater Sci Lett. 1998;17:303–5.
7. Domenech SC, Lima E Jr, Drago V, De Lima JC, Borges NG Jr, Avila AOV, Soldi V. Electroless plating of nickel-phosphorous on surface-modified poly(ethylene terephthalate) films. Appl Surf Sci. 2003;220:238–50.
8. Garcia-Gabaldon M, Perez-Herranz V, Garcia-Anton J, Guinon JL. Electrochemical study of activating solution for electroless plating of polymers. J Appl Electrochem. 2007;37:1145–52.
9. Mai TT, Schultze JW, Staikov G. Relation between surface preconditioning and metal deposition in direct galvanic metallization of insulating surfaces. J Solid State Electrochem. 2004;8:201–8.
10. Mai TT, Schultze JW, Staikov G, Munoz AG. Mechanism of galvanic metallization of CoS-activated insulating polymer surfaces. Thin Solid Films. 2005;488:321–8.
11. Pan CT. Selective electroless copper plating micro-coil assisted by 248 nm excimer laser. Microelectron Eng. 2004;71:242–51.
12. Charbonnier M, Romand M, Goepfert Y. Ni direct electroless metallization of polymers by a new palladium-free process. Surf Coat Technol. 2006;200:5028–36.
13. Chen D, Li Y, Lu Q, Yin J, Zhu Z. Selective silver seeding on laser modified polyimide for electroless copper plating. Appl Surf Sci. 2005;246:167–73.
14. Ma ZH, Tan KL, Kang ET. Electroless plating of palladium and copper on polyaniline films. Synth Met. 2000;114:17–25.
15. Charbonnier M, Romand M, Goepfert Y, Leonard D, Bessueille F, Bouadi M. Palladium (+2) reduction: a key step for the electroless Ni metallization of insulating substrates by a tin-free process. Thin Solid Films. 2006;515:1623–33.

16. Bhansali S, Sood DK. A novel technique for fabrication of metallic structures on polyimide by selective electroless copper plating using ion implantation. Thin Solid Films. 1995;270:489–92.
17. Yu ZJ, Kang ET, Neoh KG. Electroless plating of copper on polyimide films modified by surface grafting of tertiary and quaternary amines polymers. Polymer. 2002;43:4137–46.
18. Rytlewski P. Laser induced electroactivity of polyamide composites. Electrochim Acta. 2012;61:191–7.
19. Rytlewski P. Laser-assisted metallization of composite coatings containing copper(II) acetylacetonate and copper(II) oxide or copper(II) hydroxide. Surf Coat Technol. 2014;259:660–6.
20. Hanus F, Kolev K, Jadin A, Laude LA. Excimer laser-induced copper nanocluster formation in mixed PMMA/copper acetyloacetonate films. Appl Surf Sci. 2000;154–155:320–3.
21. Beauvois S, Renaut D, Jadin A, Laude LD, Lazzaroni R, Bredas JL. Excimer laser interaction with mixed PMMA-copper acetylacetonate films. Nucl Instrum Methods Phys Res B. 1997;131:167–71.
22. Kolev K, Jadin A, Benbakoura S, Laude LD. Excimer laser-induced modification in PMMA/Ni-acetylacetonate films for selective metallization. Appl Surf Sci. 1999;138–139:434–8.
23. Stolov A, Wrubel J, Simoff D. Thermal stability of specialty optical fiber coatings. J Therm Anal Calorim. 2016;124:1411–23.
24. Ye Q, Huang Z, Hao Y, Wang J, Yang X, Fan X. Kinetic study of thermal degradation of poly(l-lactide) filled with β-zeolite. J Therm Anal Calorim. 2016;124:1471–84.
25. Palkovska M, Slovak V, Subrt J, Bohacek J, Barbierikova Z, Brezova V, Fajgar R. Investigation of the thermal decomposition of a new titanium dioxide material. J Therm Anal Calorim. 2016;125:1071–8.
26. Zapała L, Kosinska M, Woznicka E, Byczynski Ł, Zapała W. Synthesis, spectral and thermal study of La(III), Nd(III), Sm(III), Eu(III), Gd(III) and Tb(III) complexes with mefenamic acid. J Therm Anal Calorim. 2016;124:363–74.
27. Srinivasan V, Smrtic MA. Excimer laser etching of polymers. J Appl Phys. 1986;59:3861–7.
28. Rytlewski P. Application of Nd:YAG laser in electroless metallization of polymer composites. Mater Manuf Process. 2014;29:1111–6.
29. Rytlewski P. Influence of glass fibre content on catalytic and adhesion properties of laser irradiated polyamide composites. Surf Eng. 2012;29:713–9.